

materials, followed by mixing and adding of liquid raw materials. The order of addition of the zircon to the other raw materials is not critical.

Suitable shapes for the carrier of this invention include any of the wide variety of shapes known for such catalyst supports, including pills, chunks, tablets, pieces, pellets, rings, spheres, wagon wheels, toroids having star shaped inner and/or outer surfaces, and the like, of a size suitable for employment in fixed bed reactors. Conventional commercial fixed bed ethylene oxide reactors are typically in the form of a plurality of parallel elongated tubes (in a suitable shell) about 1 to 3 inches (2.54 to 7.62 centimeters) O.D. and 15-45 feet (4.572-13.716 meters) long filled with catalyst. In such fixed bed reactors, it is desirable to employ carrier formed into a rounded shape, such as, for example, spheres, pellets, rings, tablets and the like, having diameters from about 0.1 inch (0.254 centimeter) to about 0.8 inch (2.032 centimeter).

There are many well-known methods of preparing carriers suitable for use in ethylene oxide catalysts. Some of such methods are described in, for example, U.S. Patents 4,379,134; 4,806,518; 5,063,195; 5,384,302, U.S. Patent Application 20030162655 and the like. As long as the carrier materials and method of preparation do not substantially decompose zircon, these methods can be employed to prepare the zircon modified carrier of the present invention. For example, an alpha-alumina support of at least 95 % purity (exclusive of zirconium component) can be prepared by compounding (mixing) the raw materials, extrusion, drying and a high temperature calcination. In this case, the starting raw materials usually include one or more alpha-alumina powder(s) with different properties, a clay-type material which may be added as binder to provide physical strength, and a burnout material (usually an organic compound) used in the mix to provide desired porosity after its removal during the calcination step. The levels of impurities in the finished carrier are determined by the purity of the raw materials used, and their degree of volatilization during the calcination step. Common impurities may include silica, alkali and alkaline earth metal oxides and trace amounts of metal and/or non-metal-containing additives.

Another method for preparing a carrier of this invention having particularly suitable properties for ethylene oxide catalyst usage comprises mixing zirconium silicate with boehmite alumina (AlOOH) and/or gamma-alumina, peptizing the aluminas with a mixture containing an acidic component and halide anions (preferably fluoride anions) to provide peptized halogenated alumina, forming (for example, by extruding or pressing) the peptized halogenated alumina to provide formed peptized halogenated alumina, drying the formed peptized halogenated alumina to provide dried formed alumina, and calcining the dried formed alumina to provide pills of modified alpha-alumina carrier.

The modified alpha-alumina carrier prepared by the method described above preferably has a specific surface area of at least about $0.5 \text{ m}^2/\text{g}$ (more preferably from about $0.7 \text{ m}^2/\text{g}$ to about $10 \text{ m}^2/\text{g}$), a pore volume of at least about 0.5 cc/g (more preferably from about 0.5 cc/g to about 2.0 cc/g), purity (exclusive of zirconium component) of at least 99 wt. % alpha-alumina, and median pore diameter from about 1 to about 50 microns. In this case, the modified alpha-alumina carrier comprises particles each of which has at least one substantially flat major surface having a lamellate or platelet morphology which approximates the shape of a hexagonal plate (some particles having two or more flat surfaces), at least 50 % of which (by number) have a major dimension of less than about 50 microns.

In the finished carrier of the present invention, including those prepared by the two particular methods described above as a way of illustration, zirconium silicate is present in an amount which is preferably in the range of from about 0.01 to about 10.0 % by weight, more preferably from about 0.1 to about 5.0 % by weight, and most preferably from about 0.3 to about 3.0 % based on the total weight of the finished modified alumina carrier.

While the invention is not constrained by any particular theory, the raw materials used to manufacture the carrier should not contain large amounts of reactive calcium compounds in order to minimize the reaction of these species with the added zirconium silicate, resulting in the formation of less beneficial species, particularly zirconia (ZrO_2 , also called zirconium oxide). The cumulative concentration of calcium compounds in carrier raw materials should be limited so that the fired carrier (excluding zirconium component) contains less than 2000 ppmw calcium, preferably less than 350 ppmw calcium.

In addition, certain other alkaline earth metal compounds may also promote the decomposition of zirconium silicate to zirconia. The cumulative concentration of alkaline earth metal compounds in carrier raw materials should be limited so that the fired carrier (excluding zirconium component) contains less than 500 ppmw alkaline earth metal (excluding calcium compounds), measured as the alkaline earth metal oxide.

The calcination temperature (firing temperature) of the carrier must also be controlled to limit the thermal decomposition of zircon to zirconia which occurs in the pure state at temperatures above 1540°C .

Catalysts for the production of alkylene oxide, for example ethylene oxide or propylene oxide, may be prepared on the modified supports of the present invention by impregnating the carrier with a solution of one or more silver compounds, as is well known in the art. One or more promoters may be impregnated simultaneously with the silver impregnation, before the silver impregnation and/or after the silver impregnation. In making such a catalyst, the carrier

is impregnated (one or more times) with one or more silver compound solutions sufficient to allow the silver to be supported on the carrier in an amount which ranges from about 2 to about 60 %, more preferably from about 5 to about 50 %, most preferably from about 10 to about 40 % of the weight of the catalyst.

- 5 Although silver particle size is important, the range is not narrow. Suitable silver particle size can be in the range of from about 100 to 10,000 angstroms.

There are a variety of known promoters, that is, materials which, when present in combination with particular catalytic materials, for example, silver, benefit one or more aspect of catalyst performance or otherwise act to promote the catalyst's ability to make a desired
10 product, for example ethylene oxide or propylene oxide. Such promoters in themselves are generally not considered catalytic materials. The presence of such promoters in the catalyst has been shown to contribute to one or more beneficial effects on the catalyst performance, for example enhancing the rate or amount of production of desired product, reducing the temperature required to achieve a suitable rate of reaction, reducing the rates or amounts of
15 undesired reactions, etc. Competing reactions occur simultaneously in the reactor, and a critical factor in determining the effectiveness of the overall process is the measure of control one has over these competing reactions. A material which is termed a promoter of a desired reaction can be an inhibitor of another reaction, for example a combustion reaction. What is significant is that the effect of the promoter on the overall reaction is favorable to the efficient production
20 of the desired product, for example ethylene oxide. The concentration of the one or more promoters present in the catalyst may vary over a wide range depending on the desired effect on catalyst performance, the other components of a particular catalyst, the physical and chemical characteristics of the carrier, and the epoxidation reaction conditions.

There are at least two types of promoters – solid promoters and gaseous promoters.

- 25 A solid promoter is incorporated into the catalyst prior to its use, either as a part of the carrier (that is support) or as a part of the silver component applied thereto. When a solid promoter is added during the preparation of the catalyst, the promoter may be added to the carrier before the silver component is deposited thereon, added simultaneously with the silver component, or added sequentially following the deposition of the silver component on the carrier. Examples
30 of well-known solid promoters for catalysts used to produce ethylene oxide include compounds of potassium, rubidium, cesium, rhenium, sulfur, manganese, molybdenum, and tungsten. During the reaction to make ethylene oxide, the specific form of the promoter on the catalyst may be unknown.

The catalyst prepared on the zircon-modified carrier may contain alkali metal and/or alkaline earth metal as cation promoters. Exemplary of the alkali metal and/or alkaline earth metals are lithium, sodium, potassium, rubidium, cesium, beryllium, magnesium, calcium, strontium and barium. Other cation promoters include Group 3b metal ions including lanthanide series metals. In some instances, the promoter comprises a mixture of cations, for example cesium and at least one other alkali metal, to obtain a synergistic efficiency enhancement as described in U.S. No. 4,916,243, herein incorporated by reference. Note that references to the Periodic Table herein shall be to that as published by the Chemical Rubber Company, Cleveland, Ohio, in CRC Handbook of Chemistry and Physics, 46th Edition, inside back cover.

The concentration of the alkali metal promoters in the finished catalyst is not narrow and may vary over a wide range. The optimum alkali metal promoter concentration for a particular catalyst will be dependent upon performance characteristics, such as catalyst efficiency, rate of catalyst aging and reaction temperature.

The concentration of alkali metal (based on the weight of cation, for example cesium) in the finished catalyst may vary from about 0.0005 to 1.0 wt. %, preferably from about 0.005 to 0.5 wt. %. The preferred amount of cation promoter deposited on or present on the surface of the carrier or catalyst generally lies between about 10 and about 4000, preferably about 15 and about 3000, and more preferably between about 20 and about 2500 ppmw of cation calculated on the total carrier material. Amounts between about 50 and about 2000 ppm are frequently most preferable. When the alkali metal cesium is used in mixture with other cations, the ratio of cesium to any other alkali metal and alkaline earth metal salt(s), if used, to achieve desired performance is not narrow and may vary over a wide range. The ratio of cesium to the other cation promoters may vary from about 0.0001:1 to 10,000:1, preferably from about 0.001:1 to 1,000:1. Preferably, cesium comprises at least about 10, more preferably, about 20 to 100 % (weight) of the total added alkali metal and alkaline earth metal in finished catalysts using cesium as a promoter.

Examples of some of the anion promoters which may be employed with the present invention include the halides, for example fluorides and chlorides, and the oxyanions of the elements other than oxygen having an atomic number of 5 to 83 of Groups 3b to 7b and 3a to 7a of the Periodic Table. One or more of the oxyanions of nitrogen, sulfur, manganese, tantalum, molybdenum, tungsten and rhenium may be preferred for some applications.

The types of anion promoters or modifiers suitable for use in the catalysts of this invention comprise, by way of example only, oxyanions such as sulfate, SO_4^{-2} , phosphates, for

and oxygen process conditions, which simulate typical conditions in commercial oxygen-type ethylene oxide processes where pure oxygen is added as the oxygen source. Each case provides a different efficiency but it is the rule for practically all cases that with air as the oxygen feed, lower amounts of oxygen and ethylene are used which will yield an efficiency to ethylene epoxide which is about 2 to 5 percentage points lower than that when pure oxygen is employed as oxygen source. Well known, back-mixed, bottom-agitated "Magedrive" autoclaves described in FIG 2 of the paper by J. M. Berty entitled "Reactor for Vapor Phase-Catalytic Studies," in Chemical Engineering Progress, Vol. 70, No. 5, pages 78-84, 1974, are used as one of the reactors. The inlet conditions include the following:

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Table I – Ethylene Epoxidation Inlet Process Conditions

Component	Air Process Conditions-I Mole %	Oxygen Process Conditions-I Mole %	Oxygen Process Conditions-II Mole %
Ethylene	11.0	30.0	30.0
Oxygen	7.0	8.0	8.0
Ethane	0.00-0.24	0.5	0.0
Carbon Dioxide	5.5	6.5	0.0
Nitrogen	Balance of gas	Balance of gas	Balance of gas
Parts per million Ethyl Chloride	Optimum for Efficiency	Optimum for Efficiency	Optimum for Efficiency
Parts per million Nitric Oxide	None	None	Optimum for Efficiency
Type of Reactor	CSTR	CSTR	CSTR
Amount of Catalyst	80 cc	80 cc	40 cc
Total Inlet Flow Rate	22.6 SCFH (.639961 standard cubic meter per hour)	22.6 SCFH (.639961 standard cubic meter per hour)	11.3 SCFH (.319980 standard cubic meter per hour)

The pressure is maintained at about 275 psig (pounds per square inch, gauge) (19.3391 kilograms per square centimeter) and the total flow is maintained at about 11.3 or 22.6 SCFH (Standard Cubic Feet per Hour) (.319980 or .639961 Standard Cubic Meter per Hour). SCFH refers to cubic feet per hour at standard temperature and pressure, namely, 0°C and one atmosphere. Ethyl chloride concentration is adjusted to achieve maximum efficiency. Temperature (°C) and catalyst efficiency are obtained as the responses describing the catalyst performance.

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The catalyst test procedure used for autoclaves in the Ethylene Epoxidation Process Conditions involves the following: 40 or 80 cc of catalyst is charged to the back-mixed

autoclave and the weight of the catalyst is noted. The back-mixed autoclave is heated to about reaction temperature in a nitrogen flow of 10 or 20 SCFH (.283168 or .566337 standard cubic meter per hour) with the fan operating at 1500 rpm. The nitrogen flow is then discontinued and the above-described feed stream is introduced into

the reactor. The total gas inlet flow is then adjusted to 11.3 SCFH (.319980 standard cubic meter per hour) for 40 cc of catalyst or 22.6 SCFH (.639961 standard cubic meter per hour) for 80 cc of catalyst. The temperature is adjusted over the next few hours to provide the desired percent outlet ethylene oxide and the optimum efficiency is obtained by adjusting ethyl chloride. The outlet epoxide concentration is monitored to make certain that the catalyst has reached its peak steady state performance. The ethyl chloride is periodically adjusted, and the efficiency of the catalyst to ethylene oxide and the rate of deactivation (temperature rise) is thus obtained. In determining activity and efficiency, the process and catalyst should be under steady state conditions.

The standard deviation of a single test result reporting catalyst efficiency in accordance with the procedure described above is about 0.3 % efficiency units. The typical standard deviation of a single test result reporting catalyst activity in accordance with the procedure described above is about 1.2°C. The standard deviation, of course, will depend upon the quality of the equipment and precision of the techniques used in conducting the tests, and thus will vary. These standard deviations are believed to apply to the test results reported herein.

The properties of the starting carrier materials and the specifics of their modifications are detailed in Table II. Table III sets forth the specifics of the catalyst preparations on the carriers of Table II, including catalyst compositions.

20 CARRIER PREPARATIONS

Carriers of the examples were prepared in the following manner. Zirconium silicate (if used) was added with other solid raw materials to obtain a dry mixture. In all cases where zircon was used, it was introduced in a powder form with a median particle size of about 130 microns. Liquids and additional dry raw materials (optional) were then added.

The amounts of such additives are expressed as percentages by weight of the starting dry mixture. Water was also added in an amount sufficient to obtain an extrudable mixture. Such amount depends on a number of factors, such as ambient humidity, hydration level of the raw materials, etc. Unless otherwise noted in the following descriptions, the mixture was extruded as cylinders with a single opening along the axis, or as multi-partitioned cylinders. After drying, the extruded greenware was fired to alpha-alumina under conditions chosen to ensure complete conversion of the extrudates to alpha-alumina. Firing temperatures between 1000°C and 1400°C and firing times from 45 minutes to 5 hours were used. Outer diameter dimensions of the fired greenware were 0.31-0.35 inches (.7874-.889 centimeters), cylinder

lengths 0.29-0.34 inches (.7366-.8636 centimeters), and the wall thickness of the multi-partitioned cylinders no greater than 0.075 inches (.1905 centimeters). Physical

properties and the approximate weight percent of zircon in the modified carriers and comparative carriers are given in Table II. All percentages in the following descriptions are in weight percent.

5. **Table II: Carrier Properties**

Carrier ID	A	B	C	D	E	F	G	H	I	J	K	L	M
Surface Area (m ² /g)	1.04	1.18	1.29	1.01	1.46	1.19	0.49	0.63	0.94	0.60	0.52	0.49	0.54
Packing Density (lb/ft ³)	32.5	33.1	34.2	34.6	25.5	24.9	27.4	25.5	25.4	31.4	32.5	30.4	30.5
(kilograms per cubic meter)	(520.600)	(530.211)	(547.831)	(554.239)	(408.471)	(398.860)	(438.906)	(408.471)	(406.869)	(502.980)	(520.600)	(486.961)	(488.563)
Pore Volume (cc/g)	0.68	0.63	0.61	0.66	0.76	0.80	0.59	0.77	0.92	0.53	0.56	0.63	0.65
Zircon Target (Wt.%)	2	0	1	0	2	0	3	0.3	0	2	0	2	0

Carrier A was prepared from calcined alumina which originally contained 0.06 wt. % CaO. The alumina was combined with a 10 % acetic acid solution and heated at 100°C for 15 minutes with stirring, then filtered and vacuum rinsed twice with hot deionized water.

- 10 The leached alumina was dried overnight at 100°C and was found to contain 0.03 % CaO. A dry mixture was prepared from 71.1 % of the leached alumina, 22.8 % organic pore-forming burnout, 4.5 % extrusion aids, <1 % flux material and 1.4 % granular zircon. 2.1 % additional extrusion aid and <1 % surfactant were added as aqueous slurries with sufficient water to form an extrudable blend. This blend was extruded, dried and fired to alpha alumina. The final
- 15 sample contained about 2 % zircon.

Comparative Carrier B was prepared in a similar manner as Carrier A except that no zircon was added.

Carrier C was prepared by blending a dry mixture of 79.2 % pseudoboehmite, 19.8 % gamma-alumina and 1 % granular zircon. 5.5 % formic acid and 4.6 % ammonium

20 bifluoride were added as aqueous solutions with sufficient water to form an extrudable blend. After mixing, the blend was extruded, dried and fired to alpha-alumina. The final sample contained about 1 % zircon.

Comparative Carrier D was prepared using the same procedure as that given above for Carrier C except that no zircon was added.

- 25 Carrier E was prepared by blending a dry mixture of 75.5 % gibbsite, 22.5 % pseudoboehmite, and 2.0 % granular zircon. To this dry mixture was added

31.4 % graphite with a particle size less than 600 microns. 1.7 % Ammonium fluoride,
2.0 % magnesium nitrate hydrate and 1.2 % nitric acid were then added as aqueous solutions

dihydrate (reagent grade) to the aqueous ethylenediamine solution such that the temperature of the solution does not exceed 40°C, (3) slowly adding 1.98 parts of silver oxide, and (4) adding 0.40 parts of monoethanolamine (Fe and Cl free).

5 The carrier was impregnated in an appropriately sized glass or stainless steel cylindrical vessel which was equipped with suitable stopcocks for impregnating the carrier under vacuum. A suitable separatory funnel which was used for containing the impregnating solution was inserted through a rubber stopper into the top of the impregnating vessel. The impregnating vessel containing the carrier was evacuated to approximately 1-2" (2.54-5.08 centimeters) mercury absolute for 10 to 30 minutes, after which the impregnating solution was slowly added
10 to the carrier by opening the stopcock between the separatory funnel and the impregnating vessel. After all the solution emptied into the impregnating vessel (~15 seconds), the vacuum was released and the pressure returned to atmospheric. Following addition of the solution, the carrier remained immersed in the impregnating solution at ambient conditions for 5 to 30 minutes, and was thereafter drained of excess solution for 10 to 30 minutes.

15 The silver-impregnated carrier was then roasted as follows to effect reduction of silver on the catalyst surface. The impregnated carrier was spread out in a single layer on stainless steel wire mesh trays then placed on a stainless steel belt (spiral weave) and transported through a 2" x 2" (5.08 x 5.08 centimeter) square heating zone for 2.5 minutes, or equivalent conditions were used for a larger belt operation. The heating zone was maintained at 500°C by passing hot
20 air upward through the belt and about the catalyst particles at the rate of 266 SCFH (7.53228 standard cubic meters per hour). After being roasted in the heating zone, the catalyst was cooled in the open air to room temperature and weighed.

Next, the silver-impregnated carrier was vacuum impregnated with a second silver impregnation solution containing both the silver oxalate amine solution and the catalyst
25 promoters. The second impregnation solution was composed of all of the drained solution from the first impregnation plus a fresh aliquot of the first solution, or a new solution was used.

The promoters, in either aqueous solution or neat form, were added (in the ascending numeric order listed in Table III) with stirring. In Catalysts 3 through 10, two equivalents of diammonium ethylenediaminetetraacetic acid (EDTA) were added with the manganese
30 promoter in order to stabilize the manganese in the impregnation solution. In Catalysts 11 and 12, one excess equivalent of diammonium EDTA was added for the same purpose.

The impregnation, draining and roasting steps for this second impregnation were carried out analogously to the first impregnation.



Table III: Catalyst Preparations – Part 4

Catalyst No.	13	14	15
Carrier No.	M	J	K
Promoter 1	CsOH	KNO ₃	KNO ₃
Promoter 2	Cs ₂ SO ₄	K ₂ Mn(EDTA)	K ₂ Mn(EDTA)
Promoter 3	Cs ₂ MoO ₄		
Promoter 4	Mn(NO ₃) ₂		
Chelating Agent	(NH ₄) ₂ H ₂ (EDTA)	(NH ₄) ₂ H ₂ (EDTA)	(NH ₄) ₂ H ₂ (EDTA)
Total Wt.% Silver	32.9	31.5	32.7
Promoter 1; ppm	373 Cs	957 K	965 K
Promoter 2; ppm	83 SO ₄	144 Mn	144 Mn
Promoter 3; ppm	9 Mo		
Promoter 4; ppm	33 Mn		

In Tables IV through X "Mlb EO/CF" denotes units of 1000 pounds (453.592 kilograms) of ethylene oxide produced per cubic foot (meter) of catalyst.

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Example 1 – Catalyst 1 and Comparative Catalyst 2

Eighty cubic centimeters of each catalyst (61.4 g.) was charged to an autoclave reactor and tested under Air Process Conditions - I (Table I). Outlet ethylene oxide was set to 1.2 mole percent until day 6 when it was increased to 1.4 mole percent. Table IV compares the performance of the catalyst containing 2 wt. % zircon (Catalyst 1) with one containing no zircon (Comparative Catalyst 2). The catalyst containing zircon has higher initial efficiency and lower initial temperature (higher activity).

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Table IV: Example 1 Catalyst Performance

	Efficiency %			Temp. °C		
	2 Mlb EO/CF	5 Mlb EO/CF	7 Mlb EO/CF	2 Mlb EO/CF	5 Mlb EO/CF	7 Mlb EO/CF
Catalyst 1	76.4	74.7	71.7	260	269	280
Catalyst 2 (comparative)	74.8	73.4	71.6	266	274	281

Example 2 – Catalyst 3 and Comparative Catalyst 4

An equal weight (63.5 g.) of each catalyst was charged to an autoclave reactor and tested under the Air Process Conditions-I described in Table I. The outlet ethylene oxide was set to 1.4 mole percent and temperature and efficiency monitored as the catalysts aged.

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Example 7 – Catalyst 14 and Comparative Catalyst 15

Thirty cubic centimeters (26.8 g. for Comparative Catalyst 14 and 26.1 g. for Catalyst 15) of each catalyst was charged to an autoclave reactor and tested under Oxygen Process Conditions - II (Table I). After initial operation at temperatures between 220 and 255 °C, conditions were adjusted for a total flow of 21.3 SCFH (.603149 standard cubic meter per hour), and temperature was controlled to maintain 1.2 mole % outlet ethylene oxide. Initial efficiency of Catalyst 14, which contains zircon is higher than that of Comparative Catalyst 15, and the efficiency decline rate is reduced.

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Table X: Example 7 Catalyst Performance

	Efficiency %			Temp. °C		
	Day 12	Day 16	Day 21	Day 12	Day 16	Day 21
Catalyst 14	86.3	86.5	86.1	246	247	248
Catalyst 15 (comparative)	84.5	84.3	83.4	247	248	250

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